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Rate constants for total relaxation from the rotational levels $J = 7.5$, 20.5, 31.5 and 40.5 in NO$(X\,^2\Pi_{1/2},\ v = 2)$ in collisions with He, Ar and N_2: a comparison between experiment and theory

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Abstract

Using the infrared–ultraviolet double resonance (IRUVDR) technique, rate coefficients have been measured for the relaxation of NO$(X^2\Pi_{1/2},\ v = 2,\ J = 7.5$, 20.5 and 31.5) in collisions with He, Ar, N_2 and NO itself. For relaxation from levels $J = 31.5$ and 40.5, rates were measured by a new method in which the IRUVDR method was implemented instantly on NO molecules formed by photodissociation of NO_2 at 355 nm. The rate coefficients for collisions with He, Ar and N_2 are found to decrease at high J, with the decrease least with He. The experimental results for NO–He and NO–Ar are shown to agree well with those from coupled states quantum scattering calculations on ab initio potential energy surfaces. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

In recent years, optical–optical double resonance techniques have been widely used to measure two kinds of rate coefficient for collisionally induced rotational energy transfer: (i) those for *total* transfer out of a specific rovibrational level, and (ii) those for *state-to-state* transfer between specific initial and final levels. Collisions involving NO$(X\,^2\Pi_\Omega)$ have been the subject of a large number of experimental investigations [1–11], including several from this laboratory [4–7,10]. In part, this emphasis on NO is a result of its favourable spectroscopic properties. Thus, it can be excited to specific rotational levels of low vibrational states ($v \leqslant 3$) by direct infrared absorption [1–7,10] or to levels of higher vibrational states, e.g., $v = 20$, by stimulated emission pumping [8,9]. Moreover, the subsequent fate of these excited molecules can then be followed by means of laser-induced fluorescence (LIF) [4–10] or resonance-enhanced multiphoton ionization (REMPI) [1–3,11] techniques. The increase in experimental information on rotational energy transfer in NO has been paralleled by progress in theory [9–19]. Collisions involving NO$(X\,^2\Pi_\Omega)$, particularly those with the rare-gas atoms He and Ar, where accurate ab initio potential surfaces are available [13], have become an interesting and challenging prototype for encounters involving molecular radicals in $^2\Pi_\Omega$ states.

Our experimental work in Birmingham [4–7,10], including that reported in the present Letter, has

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employed the infrared–ultraviolet double resonance (IRUVDR) technique to study rotational energy transfer in NO–rare-gas collisions. A pulsed, tunable, infrared 'pump' laser is used to excite NO molecules to a specific rotational level in either the $v = 2$ or $v = 3$ vibrational level of the $X\,^2\Pi_\Omega$ electronic ground state. A tunable dye laser then excites LIF from the rovibrationally excited molecules via transitions in the $A\,^2\Sigma^+$–$X\,^2\Pi$ system. Rate coefficients for *total* relaxation are determined by tuning this 'probe' laser to a transition from the rovibrational level directly populated by IR absorption, and observing the variation of the LIF signal intensity as the time delay between the pulses from the pump and probe lasers is varied. Alternatively, the delay between the two laser pulses can be fixed to correspond to a small fraction of the time between collisions and the frequency of the probe laser scanned to record a LIF spectrum. The line intensities in this spectrum reflect the concentrations in levels populated in collisions of the NO molecules in the level originally excited and hence *state-to-state* rate coefficients can be determined.

The IRUVDR method as just described has one major drawback. The excited states that can be initially selected are limited by the thermal populations of rotational levels in $NO(X\,^2\Pi_\Omega,\ v = 0)$ and the optical selection rules for the IR transitions. This restriction is particularly apparent in the extensive measurements that we have made on rotational energy transfer at temperatures down to 7 K [7,10]. In the experiments reported in the present Letter, the range of data on rotational energy transfer in $NO(X\,^2\Pi_\Omega)$ has been extended to rotational levels up to $J = 40.5$. This has been achieved by performing IRUVDR experiments on NO immediately after its formation in the photodissociation of NO_2 at 355 nm. This photolytic process creates $NO(X\,^2\Pi_\Omega)$ in rotational levels in $v = 0$ and $v = 1$ up to the energetically accessible limits [20–23]. In our experiments, IR pulses from a difference-frequency laser source have excited molecules to $v = 2,\ J = 31.5$ and $v = 2,\ J = 40.5$ and kinetic experiments have been performed to measure rate coefficients for total removal from these levels in collisions with He, Ar and N_2. These results are compared with new, conventional IRUVDR measurements on the rotational relaxation of NO from levels $J = 7.5$, 20.5 and 31.5 and all these results are compared with the results of quantum scattering calculations performed on ab initio potential energy surfaces.

As well as fundamental interest, in particular the investigation of whether the theoretical results continue to match experiment for high values of J, where the spacing between neighbouring rotational levels approaches $k_B T$, the investigation of rotational energy transfer at high J is important in respect of various aspects of atmospheric chemistry. Some evidence for a decrease in the total rate for rotational relaxation with increasing rotational quantum number comes from the observation of emission from high rotational levels of NO in the thermosphere [24,25]. The absence of a thermalised distribution over rotational levels points to the possibility of a decrease in the rate of rotational relaxation with increasing rotational quantum number. Further indirect evidence for the dependence of the total rate of rotational relaxation on the initial rotational state comes from line broadening measurements on transitions in the (2, 0) overtone band in the ground state of NO [26,27]. With increasing rotational quantum number, a slight decrease was observed in the parameter which quantifies line-broadening and which can often be correlated with the rate coefficients for rotational relaxation.

2. Experimental

The experiments were performed using the IRUVDR technique. Pulses of tunable IR radiation were generated by difference frequency mixing the output of a Nd:YAG pumped dye laser with the fundamental wavelength of the pump laser (Continuum ND8010/6000) in a $LiNbO_3$ crystal. To excite molecules to $(v = 2,\ \Omega = 1/2,\ J)$ the frequency of this pump laser was tuned into resonance with a selected line in the R branch of the $(\Omega = 1/2 \leftarrow 1/2)$ sub-band of the (2, 0) first vibrational overtone band at ca. 2.6 μm. The pulse energy of the IR radiation was in the range 1.5–2.0 mJ and the bandwidth of the laser output was ca. 0.1 cm^{-1}. The frequency of the IR laser was fine-tuned to the appropriate transition with the aid of a spectrophone containing 50 Torr of NO. Tunable UV probe radiation, with a bandwidth of ca. 0.4 cm^{-1}, was produced by frequency doubling the output of an excimer-pumped dye laser (Lambda-Physik, FL2002). LIF was excited by tuning this UV probe radiation to an appropriate transition in the (0, 2) band of the NO $A\,^2\Sigma^+ – X\,^2\Pi$ system at ca. 247 nm.

Experiments on the highest rotational levels ($J =$ 31.5 and 40.5) required the initial photolysis of NO_2 to generate rotationally hot NO molecules in the ground vibrational state. For this purpose, laser radiation was generated at 355 nm by sum frequency mixing the fundamental and doubled output of a Nd:YAG laser (Spectron, SL 803). Typical pulse energies of ca. 20 mJ and a bandwidth of 0.1 cm^{-1} were obtained.

The beams from the IR and UV lasers counter-propagated along the axis of a cylindrical Pyrex cell with a CaF_2 window mounted on each end. The photomultiplier, interference filter and a collecting lens were mounted in a central housing which was clamped to this cell. The equipment for controlling the firing of the lasers and for recording, accumulating and analysing the LIF signals was the same as that described by Frost and Smith [28].

Conventional IRUVDR experiments were carried out to measure the total rates of rotational relaxation from NO($X\,^2\Pi_{1/2}$, $v = 2$, $J = 7.5$, 20.5 and 31.5) in collisions with He, Ar, N_2 and NO. In these experiments, the IR pump laser was first tuned to the appropriate line in the (2, 0) vibrational overtone band using the spectrophone. Then a short delay was set between the pump and probe pulses and the UV laser was scanned to bring its frequency into resonance with the appropriate line in the $A\,^2\Sigma^+ – X\,^2\Pi(0, 2)$ band.

IRUVDR experiments on the NO produced from photolysis of NO_2 were carried out to measure the total rates of rotational relaxation from NO($X\,^2\Pi_{1/2}$, $v = 2$, $J = 31.5$ and 40.5) in collisions with He, Ar, N_2. Tuning the lasers was now rather more difficult. As mentioned above, for measurements on NO($X\,^2\Pi_{1/2}$, $v = 2$, $J = 31.5$), the correct IR pump frequency could be located using the spectrophone. In addition, a LIF spectrum from NO($X\,^2\Pi_{1/2}$, $v = 2$) could be taken at a time delay corresponding to ca. 1 collision in order to locate the $A\,^2\Sigma^+ – X\,^2\Pi_{1/2}(0, 2)$ transitions from higher, collisionally populated, rotational levels up to $J = 37.5$. With the frequency of the UV probe laser fixed on the line from the $J = 37.5$ level, the frequency of the pump laser was then scanned to wavelengths where the (2, 0) R-branch IR transition to $J = 40.5$ was expected, again at a delay corresponding to ca. 1 collision. A LIF signal was detected when the IR laser was in resonance with the line promoting molecules to the $J = 40.5$ level. This was confirmed by subsequently tuning the UV probe laser to the $A\,^2\Sigma^+ – X\,^2\Pi_{1/2}(0, 2)$ transition from this level at short time delays. The kinetic experiments in which the time delay between the pulses from the pump and probe lasers was varied were then performed. In the three laser experiments, the time delay between the pulse from the laser photolysing NO_2 and that from the IR pump laser was < 100 ns.

In all experiments, the time delay between the pump and probe laser pulses was varied with a delay generator (Stanford DG535) and the resulting LIF signal was detected. To discriminate against scattered light from the probe laser, the fluorescence was observed using a solar blind photomultiplier tube (Hamamatsu R801), through a quartz window and an interference filter (Corion, FWHM 10 nm) centred at 228 nm, which isolated the fluorescence in the (0, 0) band of the $A\,^2\Sigma^+ – X\,^2\Pi$ system at ca. 226 nm.

The dependence of the observed rate coefficients on the relative polarisations of the lasers was examined by rotating the plane of polarisation of the probe laser through 90° from its usual orientation using a Fresnel rhomb. The measured rate coefficients were found to be independent of this change within the error limits of the measurements. This confirmed that our measurements yield rates of rotational energy transfer and do not contain a significant component due to re-orienting collisions without change of rotational level.

3. Experimental results

The decay in the LIF signals as a function of time for a given gas mixture was fitted to an exponential function from which a pseudo-first-order rate coefficient was obtained. Examples of such fittings for NO($X\,^2\Pi_{1/2}$, $v = 2$, $J = 40.5$) in mixtures containing different partial pressures of helium are shown in Fig. 1. A series of such measurements was carried out and the first-order rate coefficients were plotted

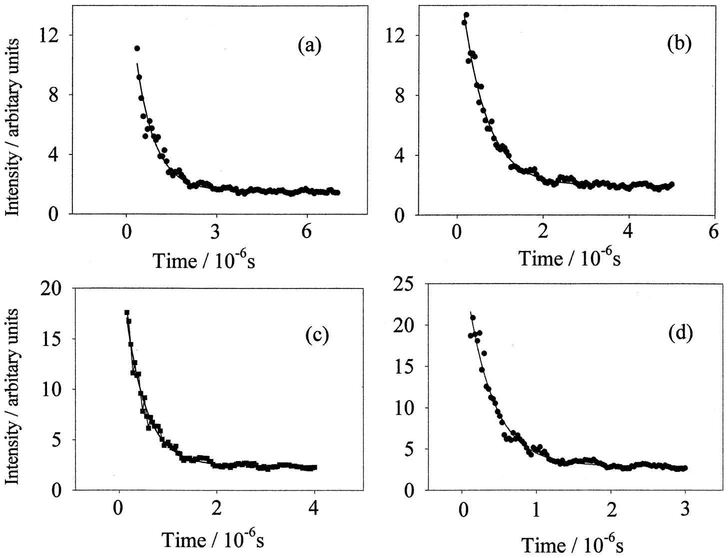

Fig. 1. Traces of LIF signal from NO($X\,^2\Pi_{1/2}$, $v = 2$, $J = 40.5$) versus time recorded from NO produced in the photolysis of NO_2 at 355 nm. All mixtures contained 20 mTorr of NO_2 in (a) 221, (b) 301, (c) 400, and (d) 507 mTorr He.

against the concentration of collision partner to yield, from the gradient, the second-order rate coefficient for *total* rotational relaxation from that particular level in collisions with the selected collision partner. Fig. 2 shows one such plot, and the measured second-order rate constants are listed in Table 1. Strictly, because the population in the observed level decays to its equilibrium value, the measurements yield the sum of the rate coefficients for relaxation out of and into the observed level. However, only for the lower levels studied here was it necessary to correct for the reverse process, as described in earlier papers [4–7,10].

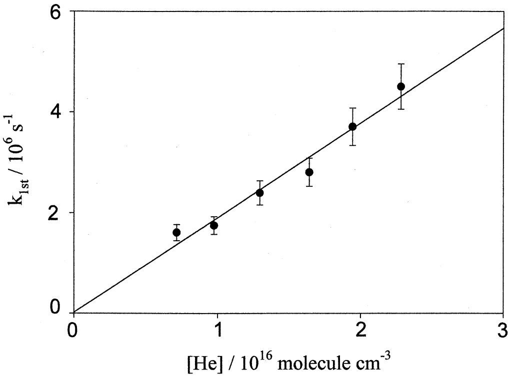

Fig. 2. Plot of the first-order rate coefficients obtained from the LIF decay traces associated with relaxation of NO($X^2\Pi_{1/2}$, $v = 2$, $J = 40.5$) plotted against the concentration of helium added to 20 mTorr of NO_2.

The derived second-order rate coefficients for relaxation by He, Ar and N_2 from different initial rotational levels are presented graphically in Fig. 3. Two general features are apparent. First, the rate coefficients show a significant, if small decrease with increasing rotational quantum number. Second, this change is least for helium as collision partner. Further, we note that the 17% decrease in the rate coefficient for relaxation by Ar in going from $J = 7.5$ to $J = 20.5$ is very similar to the 14% decrease in the collision-broadening parameters measured by Pine [27] in going from $J = 7.5$ to $J = 17.5$.

Table 1 lists two values of the rate coefficients for relaxation from $J = 31.5$, one from conventional IRUVDR experiments the other from experiments in which NO was generated in a non-thermal distribution by photolysis of NO_2 at 355 nm. In the latter case, the NO molecules will be created with a non-thermal translational distribution, their average translational energy being equivalent to ca. 460 cm^{-1}, about twice the thermal value at 298 K. The agreement between the two derived values of the rate coefficients suggest that this makes little difference

Table 1
Rate coefficients ($k/10^{-10}$ cm^3 molecule^{-1} s^{-1}) for relaxation from NO($X\,^2\Pi_{1/2}$, $v = 2$, $J = 7.5$, 20.5, 31.5 and 40.5) in collisions with He, Ar, N_2 and NO

Collision partner	$J = 6.5$[a]		$J = 7.5$		$J = 20.5$		$J = 31.5$[b]		$J = 40.5$	
He	$(3.1_6 \pm 0.3)$	[8]	(3.0 ± 0.3)[c]	{3}[d]	$(2.4_5 \pm 0.3)$	{3}	(2.1 ± 0.3)	{2}	(2.2 ± 0.3)	{2}
	$(2.3_5 \pm 0.2)$	[3(b)]			2.77[e]		2.43[e]		2.12[e]	
	2.30[e]									
Ar	(1.9 ± 0.2)	[3(b)]	(3.4 ± 0.2)	{2}	(2.8 ± 0.3)	{2}	$(1.7_5 \pm 0.2)$	{3}	(1.3 ± 0.2)	{3}
	2.74[e]				2.25[e]		(2.0 ± 0.3)	{2}	1.23[e]	
							1.60[e]			
N_2	(3.5 ± 0.5)	[3(b)]	(4.6 ± 0.5)	{3}	(4.4 ± 0.5)	{4}	(4.0 ± 0.4)	{2}	(2.5 ± 0.3)	{2}
NO	(3.8 ± 0.2)	[3(b)]	(4.2 ± 0.5)	{2}	(4.4 ± 0.3)	{2}	(3.5 ± 0.4)	{2}	–	

[a] The rate coefficients in this column are from earlier work and are included for comparison.
[b] The upper values were obtained from conventional IRUVDR experiments, the lower values from experiments in which NO was generated by 355 nm photodissociation of NO_2.
[c] Cited errors correspond to two standard deviations.
[d] Number of individual series of experiments.
[e] Theoretical calculations (present Letter), exclusive of rate for $e \to f$ transfer within the initially populated rotational level.

to the efficiency of rotational energy transfer. In the case of NO produced in $v = 0$, $J = 40.5$, the translational energy will be about half the thermal value. We have assumed that the resultant non-thermal distribution of collision energies makes no significant difference to the rate coefficients for relaxation.

4. Theoretical calculations

The theoretical rate scattering calculations follow the formalism we have presented in detail earlier [10,12–14]. To avoid repetition we shall repeat here only those details which bear directly on our new results.

We have used our earlier CEPA [29–31] calculations [18,19] of the two potential energy surfaces (PES), $V_{A'}$ and $V_{A''}$, which arise when a noble-gas atom interacts with an NO molecule in its $^2\Pi$ ground state [13]. In the scattering calculations it is most convenient to use the average and the half-difference of the two PES, namely [13]

$$V_{\rm sum}(R,\theta) = 0.5\left[V_{A''}(R,\theta) + V_{A'}(R,\theta)\right], \qquad (1a)$$

and

$$V_{\rm dif}(R,\theta) = 0.5\left[V_{A''}(R,\theta) - V_{A'}(R,\theta)\right]. \qquad (1b)$$

The total wavefunction of the NO–noble-gas system is then expanded as a sum of products of the molecular electronic–rotational wavefunctions, multiplied by functions which describe the orbital motion of the noble-gas collision partner with respect to the diatomic molecule. Collision-induced transitions between any pair of levels, at least one of which is described in this intermediate coupling regime, will be induced by both the average and difference potentials [12,14,32]. The extent of the cross-coupling of these two potentials will be governed by the degree of mixing of the pure Hund's case (a) rotational basis states of the NO molecules [14,18,19,32].

To calculate the rotationally inelastic cross sections based on these PESs we used the Hibridon 4 package. [1] In the present calculations, the coupled states (CS) approximation [12], which has been shown previously [18,19] to be accurate for collisions of NO($X\,^2\Pi$) with both He and Ar, was used. As before, the NO molecule was assumed to be a rigid rotor with a bond distance equal to the average

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[1] HIBRIDON is a package of programs for the time-independent quantum treatment of inelastic collisions and photodissociation written by M.H. Alexander, D.E. Manolopoulos, H.-J. Werner, B. Follmeg, with contributions by P.F. Vohralik, D. Lemoine, G. Corey, B. Johnson, T. Orlikowski, W. Kearney, A. Berning, A. Degli-Esposti, C. Rist, P. Dagdigian. More information and/or a copy of the code can be obtained from the website http://www-mha.umd.edu/ ~ mha/hibridon.

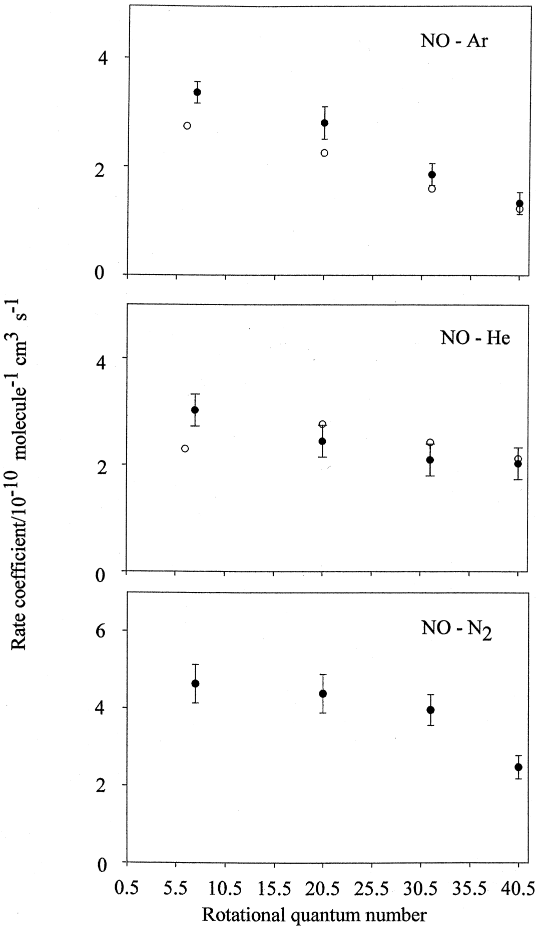

Fig. 3. Second-order rate coefficients for relaxation of NO($X^2\Pi_{1/2}$, $v = 2$) from selected rotational levels J plotted against J. The filled symbols represent the experimental data, the open symbols the results of the quantum scattering calculations described in the text.

value in the $v = 2$ vibrational state. Scattering calculations were carried out on a fixed grid of > 120 total energies, where the total energy is the sum of the energy of the initial internal state and the collision energy. Subtraction of the internal energy then transformed these results to cross-sections as a function of collision energy [10]. Thermal state-to-state rate coefficients were obtained from the inelastic integral cross-sections by multiplication of the cross-sections by the relative velocity and subsequent integration over a Maxwellian velocity distribution at 300 K. Finally, the results were summed over all final states to recover rate coefficients for total removal from the initially selected rotational level.

The theoretical results are compared with the experimental rate coefficients in Fig. 3.

5. Discussion

For lower rotational levels, the present experimental results can be compared with the rate coefficients measured previously for NO($v = 2$, $J = 6.5$) by Islam et al. [5] and for NO($v = 3$, $J = 6.5$) by James et al. [10] (see Table 1). James et al. only reported a room temperature rate coefficient for relaxation induced by collisions with He. It is in excellent agreement with our result for $v = 2$, $J = 7.5$. In most cases, agreement with the rate coefficients obtained by Islam et al. is quite good, although their rate coefficients are generally slightly smaller than the present values with a significant disagreement in the case of NO–Ar. Table 1, as well as Fig. 3, compares the theoretical and experimental rate coefficients for total removal by Ar and He. The agreement is excellent, both in absolute magnitude and in variation with the initially pumped level.

The rate coefficients measured in the present work do demonstrate that at higher rotational levels the rates of total rotational energy transfer do diminish, albeit slightly, for the range of levels up to $J = 40.5$. In the highest rotational level studied ($J = 40.5$), the rotational period of an isolated NO molecule is 0.24 ps. During collisions between NO and Ar and between NO and N_2 at the mean relative speed corresponding to 298 K, the intermolecular separation will change by only about 1.5 Å during this rotational period. Consequently, during its interaction with these collision partners, the NO molecule will undergo a substantial fraction of a full rotation with the result that the intermolecular potential will be substantially averaged over orientations which is likely to lower the probability of rotational energy transfer. With He as the collision partner, the mean relative speed is greater, by a factor > 2, and less averaging will occur. This may explain why the rate coefficients for He show less sensitivity to the initial value of the NO rotational quantum number.

Table 2
Average loss of rotational angular momentum in inelastic collisions of NO($X^2\Pi_{1/2}$, $v = 2$, $J = 20.5$, 31.5 and 40.5) in collisions with He and Ar at 300 K[a]

Collision partner	$J = 20.5$	$J = 31.5$	$J = 40.5$
He	−2.1	−2.5	−2.6
	3.2	3.2	3.0
Ar	−3.0	−2.6	−2.1
	3.7	3.1	2.4

[a] The first entry refers to $\langle \Delta J \rangle$ and the second to $\langle |\Delta J| \rangle$; see Eqs. (2a) and (2b). In both cases the calculation include transfer from the initially populated level to all rotational levels in both spin–orbit manifolds.

It is worthwhile to determine the average loss of rotational angular momentum per collision (Table 2), which can be defined as

$$\langle \Delta J \rangle_J = \sum_{J'} (J - J') k_{J \to J'} \Big/ \sum_{J'} k_{J \to J'} , \qquad (2a)$$

and

$$\langle |\Delta J| \rangle_J = \sum_{J'} |(J - J')| k_{J \to J'} \Big/ \sum_{J'} k_{J \to J'} . \qquad (2b)$$

We observe that for collisions with Ar, the average changes in rotational quantum number decrease as J increases. This reflects the increasing size in the rotational energy spacing with increasing J. Collisions with the faster moving He atom are more impulsive, and hence less sensitive to the energy loss. Consequently, for collisions with He, the average changes in rotational quantum number show little variation with J, even up to $J = 40.5$. Experimental rate coefficients for state-to-state rotational energy transfer will be reported in a future publication.

The present experimental results, obtained using a novel variant of the IRUVDR technique, substantially extend the range of rotational levels in NO($X^2\Pi_\Omega$) for which rate coefficients for relaxation are available. Nevertheless, the upper limit of the range, $J = 40.5$, falls some way short of the rotational states (up to $J \approx 100$) which are populated in the thermosphere and observed via emission measurements [24,25]. The mechanism proposed [33] for the formation of these molecules, namely the reaction of translationally excited N(^{4}S) atoms with O_2, seems unpromising from the point-of-view of laboratory investigations, where it is far preferable to employ an effectively instantaneous unimolecular photodissociation to produce rotationally ‘hot’ NO in a time much shorter than the average collision time. An alternative photochemical source to NO_2 is possibly NOCl [34]. However, at longer photolysis wavelengths (> 300 nm) NO is not produced in any higher J states than from NO_2. Photolysis at shorter wavelengths is accompanied by the formation of substantial concentrations of vibrationally excited NO molecules which may lead to complications in the analysis of such experiments.

An attractive alternative to such experiments is to explore the relaxation of NO in the range of J levels explored in the present experiments, but at much reduced translational temperatures. Such experiments should be possible using the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus which has been used already [7,10] to determine rate coefficients for rotational relaxation from low J levels in NO at temperatures down to 7 K. Such experiments would make it possible to examine rotational relaxation under conditions where the energy differences between neighbouring rotational levels far exceed the average collision energy and such experiments will be pursued in the future.

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